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Formation and characterization of single-step electrodeposited Cu_2ZnSnS_4 thin films: Effect of complexing agent volume

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Abstract

The Cu_2ZnSnS_4 (CZTS) thin films have been prepared on Mo-coated soda lime glass substrates at room temperature by single-step electrodeposition method. The morphological, compositional and structural characteristics of the prepared thin films have been explored. The surface morphology properties showed that the grain sizes of CZTS thin films were smaller with increasing complexing agent volume in quaternary ion solution. The chemical compositions reveal that the CZTS thin films prepared using the volume of 25 mL tri-sodium citrate are nearly stoichiometric. X-ray diffraction patterns indicate that the annealed CZTS thin films have a kesterite structure including secondary metal and metal sulfide phases. It is found that the tri-sodium citrate as complexing agent volume in quaternary ion solution affects the quality of CZTS thin films.

Keywords: Cu_2ZnSnS_4 thin film; Electrodeposition; Complexing agent; Tri-sodium citrate

1. Introduction

Chalcopyrite-type thin film solar cells are emerging as a low cost alternative for compound thin film solar cells. For example, CIGS ($Cu(In,Ga)S_2$ or $Cu(In,Ga)Se_2$) thin film solar cells are obtained

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remarkable high conversion efficiencies up to nearly 20% [1]. In spite of the high efficiencies, however, a low abundance of indium (In) in the earth's crust limits the amount of power that can be generated using these solar cells. Furthermore, the solar cells contain toxic elements such as Cd and Se, leading to an environmental problem. In these points of view, therefore, the development of new devices and use of new materials are essential.

In recent years, a Cu_2ZnSnS_4 (CZTS) thin film as an absorber layer of solar cells and CZTS solar cells have been proposed and investigated. The CZTS is a kesterite quaternary semiconductor containing elements which are non-toxic and are abundantly available on earth. Furthermore, it has a suitable optical band gap ~ 1.50 eV and a sufficient absorption coefficient of 10^4 cm^{-1} for application of solar cells [2,3]. The CZTS absorber layers are prepared by various formation methods, such as thermal evaporation [4,5], e-beam evaporation with a post sulfurization [6], sputtering [3,7,8], pulsed laser [9], electrochemical deposition [10−12], and spin coating methods [13]. Among these methods, an electrochemical deposition method is much attractive and simple formation technique. This deposition method has several advantages, such as low cost source materials, large area deposition, cheap capital equipment and room temperature growth in comparison with expensive vacuum process methods, such as evaporation, sputtering and so on.

In particular, a single-step electrodeposition method has been proposed by Kim's group to reduce the formation process [14,15]. However, the single step electrodeposition of CZTS thin films from aqueous is difficult since the reduction potential range of these metal ions is considerably large. *Ghazali et al.* used a complexing agent, which promotes deposition potentials of metal species closer and narrows the potential gap between the electrolyte elements for a better co-deposition environment, to obtain the stoichiometric metal thin films with good quality [16]. They realized that the complexing agent in the solution during the electrodeposition process improves the lifetime of deposition bath as well as quality of the deposited films such as uniformity, crystallinity and adhesion of the deposited film on the substrate. *Pawer et al.* suggests the tri-sodium citrate (Na_3-citrate) as complexing agent for fabrication of CZTS thin films during electrodeposition in quaternary electrolytic bath [15]. They presented the effect of concentration of complexing agent. However, they did not mention the detailed volume ratios for fabrication of CZTS thin films.

In this study, therefore, we investigated the effect of Na_3-citrate as complexing agent as a function of volume ratios. The CZTS thin films were formed by single-step electrodeposition method and the volume ratios of complexing agent were changed. The structural, morphological and compositional characteristics of the prepared thin films were evaluated and discussed.

2. Experimental details

Cu_2ZnSnS_4 (CZTS) thin films were deposited on Mo-coated soda lime glass substrates. Before deposition, the substrates were cleaned ultrasonically in acetone, ethanol and distilled water and dried by flowing nitrogen. A cyclic voltammetry (CV) was employed in preliminary experiments to find an optimum potential for the deposition of CZTS thin film with potentiostatic electrodeposition. All of the electrodeposition processes were performed in a Hokuto Denko model HZ-5000 Potentiostat/Galvanostat with a three electrode configuration. The electrochemical cell contains a saturated Ag/AgCl electrode as a reference electrode, a platinum (Pt) electrode as an inert counter electrode and Mo-coated substrate with a deposition area of $2\times2cm^2$ was used as the working electrode.

The CZTS thin films were prepared from aqueous electrolytic bath containing 0.02M copper (II) sulfate pentahydrate ($CuSO_4{\cdot}5H_2O$), 0.01M zinc sulfate hepthahydrate ($ZnSO_4{\cdot}7H_2O$), 0.02M tin sulfate ($SnSO_4$) and 0.02M sodium thiosulfate ($Na_2S_2O_3$) using a single step electrodeposition method at room temperature for 40 min. 0.2M tri-sodium citrate ($C_6H_5Na_3O_7$:Na_3-citrate) as complexing agent and tartaric acid ($C_4H_6O_6$) as pH control solution were used. For the formation of CZTS thin films, the volume of

Na_3-citrates were varied from 5 mL to 25mL. The pH concentration was contained to 5. The deposited films were annealed at 500 °C for 30 min in N_2 atmosphere and used for further investigations.

The structural properties of the as-deposited and annealed thin films were studied using X-ray diffractometry (XRD, Philips X-pert MPD with CuKα radiation, λ= 1.5406 Å). The surface morphological and compositional study of the formed films were performed by using field emission scanning electron microscopy (FE-SEM, Model: JSM-3000F, JEOL, Japan) attached with an energy-dispersive X-ray spectrometer (EDS) to measure the sample composition.

3. Results and discussion

To investigate the effect of Na_3-citrate, cyclic voltammogram of all electrolytes with varied Na_3-citrate as complexing agent volume were measured. The aim of cyclic voltammetry is to determine an optimal deposition potential in potentiostatic electrodeposition mode. The cyclic voltammogram of the quaternary CZTS electrolyte between the operating potential −1.5 V and 0 V were performed. The reduction peaks of all quaternary ion solution containing varied Na_3-citrate were observed in the cathodic scan at −1.05 V. It indicates that the reduction peak does not depend on the Na_3-citrate volume. The peak is attributed to the reduction of quaternary compound ions to CZTS thin film. From the peak, the optimized reduction potential was determined as − 1.05 V, allowing the continuous growth of CZTS thin films for potentiostatic electrodeposition.

3.1. Morphological properties

The surface morphology of the as-deposited and annealed CZTS thin films was investigated by using field emission scanning electron microscopy (FE-SEM). CZTS thin films were electrochemically deposited at reduction potential of −1.05 V. Fig. 1 presents FE-SEM surface micrographs of as-deposited CZTS thin films onto Mo-coated glass substrate. The insets of Figs. 1(a)–(e) displayed the enlarged each FE-SEM images. The films prepared with 5 mL complexing agent shown in Fig. 1(a) shows very dense and uniform surface roughness. When the complexing agent was 10 mL (see Fig. 1(b)), it is observed that the precursor film shows non-uniform distribution of agglomerated particles with well-defined boundaries. With increasing of complexing agent (Na_3-citrate) volume as shown in Fig. 1(c-e), the grain sizes of agglomerated particles were smaller. In particular, the particle grain sizes were almost same in the quaternary ion solution containing complexing agent volume above 15 mL.

For further morphological investigation, the as-deposited CZTS thin films were annealed at 500 ^{o}C for 30 min in N_2 ambient. The surface morphologies were almost same compared with that of as-deposited CZTS films. However, these results are some different compared with *Pawar et al.* report. They annealed the as-deposited CZTS thin films at 550 ^{o}C for 1 h in Ar ambient and their morphologies were changed (see ref. [15]). It might be the effect of annealing ambient gas and/or temperature. From these results, we realized that annealing conditions affect the surface morphologies of prepared CZTS thin films

3.2. Compositional properties

The chemical compositions of the as-deposited thin films and annealed thin films deposited with different Na_3-citrate ($C_6H_5Na_3O_7$) complexing agent volumes are shown in Fig. 2. For the as-deposited thin films (see Fig. 2(a)), when the Na_3-citrate volumes were below 10 mL, non-stoichiometric films were formed. With increasing the Na_3-citrate volume in the quaternary ion solution, the sulphur atomic percent of the films were increased.

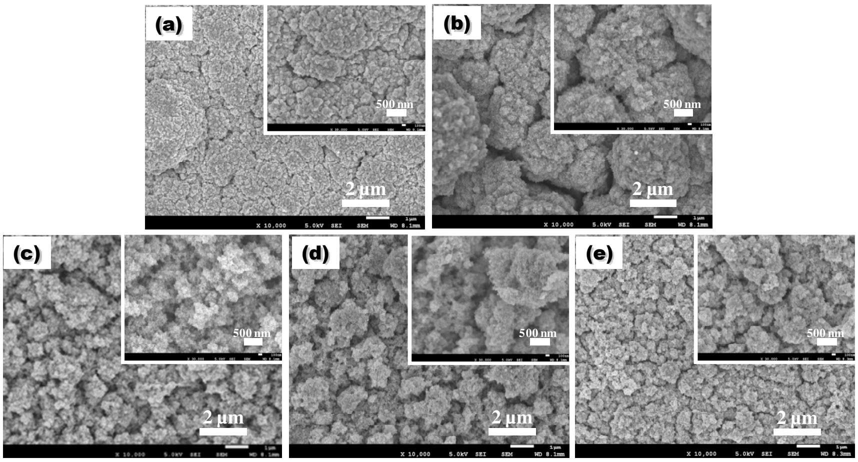

Fig. 1. FE-SEM surface micrographs for as-deposited CZTS thin films deposited from electrolytic baths with varied Na_3-citrate complexing agent volumes on Mo-coated soda lime glass substrates: (a) 5 mL, (b) 10 mL, (c) 15 mL, (d) 20 mL and (e) 25 mL

When the Na_3-citrate volume was 25 mL, nearly stoichiometric composition was obtained. It means that the optimal complexing agent exists when a CZTS thin film is prepared by single-step electrodeposition method in the fixed quaternary ion solution volume.

Fig. 2(b) shows the chemical compositions of the thin films after annealing treatment at 500 ^{o}C. The compositional results of annealed CZTS thin films showed same tendency like that of as-deposited CZTS thin films. It means that the annealing treatment does not affect the element composition in this experimental condition. Same results have been also reported by *Pawar et al.* [15]. From these EDS results, we can conclude that nearly stoichiometric CZTS thin film can be deposited by single-step electrodeposition method.

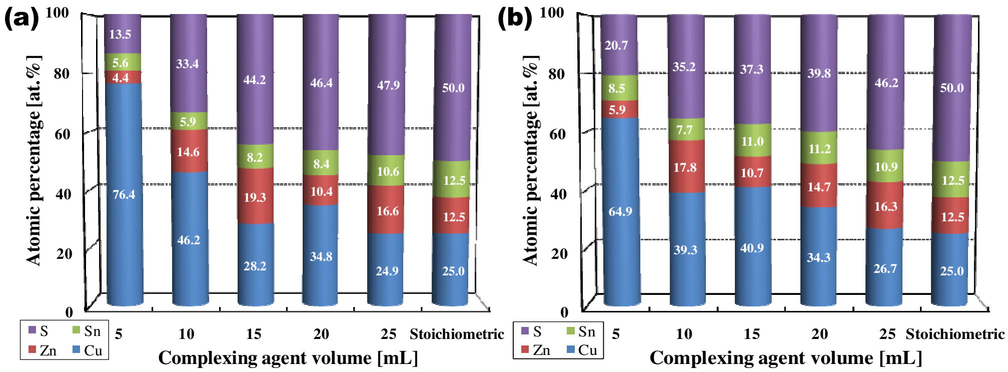

Fig.2. Pole graphs of chemical composition vs Na_3-citrate complexing agent volumes of (a) as-deposited and (b) annealed CZTS thin films

3.3. X-ray diffraction properties

For investigating the effect of Na_3-citrate complexing agent volume on the structural characteristics of CZTS thin films, the CZTS thin films were prepared with Na_3-citrate ranging from 5 to 25 mL volume.

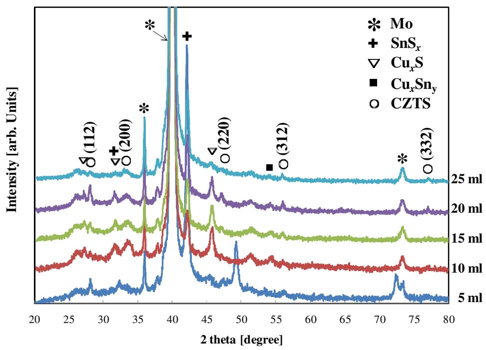

Fig.3. XRD phase diagrams of annealed CZTS thin films deposited from electrolytic baths with varied Na_3-citrate volumes

The as-prepared thin films were annealed at 500 °C for 30 min in N_2 ambient. A structural property was analyzed using XRD measurement with 2θ scanning from 20° to 80°. The XRD phase diagrams of annealed CZTS thin films deposited from quaternary ion solutions containing varied Na_3-citrate volumes on Mo-coated glass substrates are presented in Fig. 3. It is seen that all the XRD patterns consist of (112), (200), (220), (311) and (332) diffraction peaks corresponding to different crystallographic planes of Cu_2ZnSnS_4, suggesting that the films are polycrystalline with kesterite crystal structure. These results are in agreement with reports by other groups [14,15,17]. From the XRD results, evident differences by the Na_3-citrate volumes (except 5 mL) were not detected. Furthermore, some metal sulfide and other secondary phases, such as Cu_xS, SnS_x and Cu_xSn_y, were also detected. These secondary phases are often observed in CZTS thin films during the formation process, particularly for the copper-rich chalcopyrite samples [17–20]. However, the copper sulfide phase can be effectively removed by immersing the samples in KCN solution [18].

4. Conclusions

The Cu_2ZnSnS_4 (CZTS) thin films were deposited onto Mo glass substrates by single-step electrodeposition from a quaternary ion solution containing varied tri-sodium citrate as complexing agent volume. The optimal deposition potential was explored by cyclic voltammetry and the reduction potential was determined to –1.05 V at all aqueous solutions. The surface morphology properties showed that the grain sizes of CZTS thin films were smaller with increasing complexing agent volume in quaternary ion solution. The chemical compositions analyzed by EDS measurement reveal that the CZTS thin films prepared using the volume of 25 mL tri-sodium citrate are nearly stoichiometric. X-ray diffraction patterns indicate that the annealed CZTS thin films have a kesterite structure including secondary metal and metal sulfide phases. We realized that the quality of CZTS thin film strongly depends on the volume of complexing agent when the concentration is fixed.

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References

[1] Repins I, Contreras M, Egaas B, DeHart C, Scharf J, Perkins C, To B, Noufi R. 19.9%-efficient ZnO/CdS/CuInGaSe^2 Solar Cell with 81.2% Fill Factor. *Prog Photovolt.: Res Appl* 2008;**16**:235–9.

[2] Ito K, Nakazawa T. Electrical and optical properties of stannite-type quaternary semiconductor thin films. *Jpn J Appl Phys* 1988;**27**:2094–7.

[3] Tanaka T, Nagatomo T, Kawasaki D, Nishio M, Guo Q, Wakahara A, Yoshida A, Ogawa H. Preparation of Cu_2ZnSnS_4 thin films by hybrid sputtering. *J Phys Chem Solids* 2005;**66**:1978–81.

[4] Tanaka T, Kawasaki D, Nishio M, Guo QX, Ogawa H, Fabrication of Cu_2ZnSnS_4 thin films by co-evaporation. *Phys Status Solidi (c)* 2006;**3**:2844–7.

[5] Weber A, Krauth H, Perlt S, Schubert B, Kotschau I, Schorr S, Schock H. Multi-stage evaporation of Cu_2ZnSnS_4 thin films. *Thin Solid Films* 2009;**517**: 2524–6.

[6] Katagiri H, Saitoh K, Washio T, Shinohara H, Kurumadani T, Miyajima S. Development of thin film solar cell based on Cu_2ZnSnS_4 thin films. *Sol Energy Mater Sol Cells* 2001;**65**:141–8.

[7] Kobayashi T, Jimbo K, Tsuchida K, Shinoda S, Oyanagi T, Katagiri H. Investigation of Cu_2ZnSnS_4-based thin film solar cells using abundant materials. *Jpn J Appl Phys* 2005;**44**:783–7.

[8] Seol JS, Lee SY, Lee JC, Nam HD, Kim KH. Electrical and optical properties of Cu_2ZnSnS_4 thin films prepared by rf magnetron sputtering process. *Sol Energy Mater Sol Cells* 2003;**75**:155–62.

[9] Moriya K, Tanaka K, Uchiki H. Fabrication of Cu_2ZnSnS_4 Thin-Film Solar Cell Prepared by Pulsed Laser Deposition. *Jpn J Appl Phys* 2007;**46**:5780-1.

[10] Scragg JJ, Dale PJ, Peter LM. Towards sustainable materials for solar energy conversion: preparation and photoelectrochemical characterization of Cu_2ZnSnS_4. *Electrochem Commun* 2008;**10**:639–42.

[11] Ennaoui A, Lux-Steiner M, Weber A, Abou-Ras D, Kotschau I, Schock HW, Schurr R, Holzing A, Jost S, Hock R, Voss T, Schulze J, Kirbs A. Cu_2ZnSnS_4 thin film solar cells from electroplated precursors: novel low-cost perspective. *Thin Solid Films* 2009;**517**:2511–4.

[12] Jeon M, Shimizu T, Shingubara S. Cu_2ZnSnS_4 thin films and nanowires prepared by different single-step electrodeposition method in quaternary electrolyte. *Mater Lett* 2011;**65**:2364–7.

[13] Todorov TK, Reuter KB, Mitzi DB. High-efficiency solar cell with earth-abundant liquid-processed absorber. *Adv Mater* 2010;**22**:1–4.

[14] Pawar SM, Pawar BS, Moholkar AV, Choi DS, Yun JH, Moon JH, Kolekar SS, Kim JH. Single step electrosynthesis of Cu_2ZnSnS_4 (CZTS) thin films for solar cell application. *Electrochim Acta* 2010;**55**:4057–61.

[15] Pawar BS, Pawar SM, Shin SW, Choi DS, Park CJ, Kolekar SS, Kim JH. Effect of complexing agent on the properties of electrochemically deposited Cu_2ZnSnS_4 (CZTS) thin films. *Appl Surf Sci* 2010;**257**:1786–91.

[16] Ghazali A, Zainal Z, Hussein MZ, Kassim A. Cathodic electrodeposition of SnS in the presence of EDTA in aqueous media. *Sol Energy Mater Sol Cell* 1998;**55**:237–49.

[17] Cui Y, Zuo S, Jiang J, Yuan S, Chu J. Synthesis and characterization of co-electroplated Cu_2ZnSnS_4 thin films as potential photovoltaic material. *Sol Energy Mater Sol Cells* (2011) doi:10.1016/j.solmat.2011.03.013.

[18] Fernandes P, Salome P, Cunha A. Growth and Raman scattering characterization of Cu_2ZnSnS_4 thin films. *Thin Solid Films* 2009;**517**:2519–23.

[19] Schurr R., Hölzing A, Jost S, Hock R, Voβ T, Schulze J, Kirbs A, Ennaoui A, Lux-Steiner M, Weber A, Kötschau I, Schock HW. The crystallisation of Cu_2ZnSnS_4 thin film solar cell absorbers from co-electroplated Cu–Zn–Sn precursors. *Thin Solid Films* 2009;**517**:2465–8.

[20] Kamoun N, Bouzouita H, Rezig B. Fabrication and characterization of Cu_2ZnSnS_4 thin films deposited by spray pyrolysis technique. *Thin Solid Films* 2007;**515**:5949–52.